

Exploring the Conformational Behavior of Rigid Porphyrin-Quinone Systems by High-Temperature MD Simulations and Temperature-Dependent ¹H-NMR Experiments

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Abstract

Photoinduced electron transfer reactions play an important role in the primary step of the biological photosynthesis process. In an attempt to understand better the mechanism of the charge separation organic donor-acceptor molecules containing porphyrins and quinones were designed as photosynthesis models. In order to study the structure dependence of the photoinduced electron transfer twofold and fourfold bridged porphyrin-quinone systems with increasing donor-acceptor distance were synthesized (Figure 1) [1, 2, 3]. It was assumed that in these molecules the porphyrin and quinone should be linked in a rigid and well-defined orientation. To verify this assumption the conformational behavior of these systems was

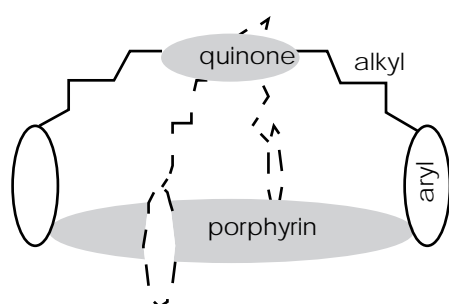


Figure 1. Schematic representation of the twofold and fourfold bridged porphyrin-quinone systems (aryl spacer: phenyl, naphthyl, biphenylenyl, anthryl; alkyl spacer: tetramethylene).

studied by high-temperature MD simulations in combination with conformational analysis of selected minimized structures [4, 5].

As an example we describe the dynamical behavior of the quadruply bridged porphyrin-quinone with naphthyl groups as aryl spacer ("naphthyl cage") (Figure 2) which was investigated by the following generally used method:

The initial structure used for MD simulation was constructed with the builder modul of INSIGHT II [6]. To stimulate the dynamics in such rigid molecules as the "porphyrin-quinone cages" during a simulation time of 1000 ps we had

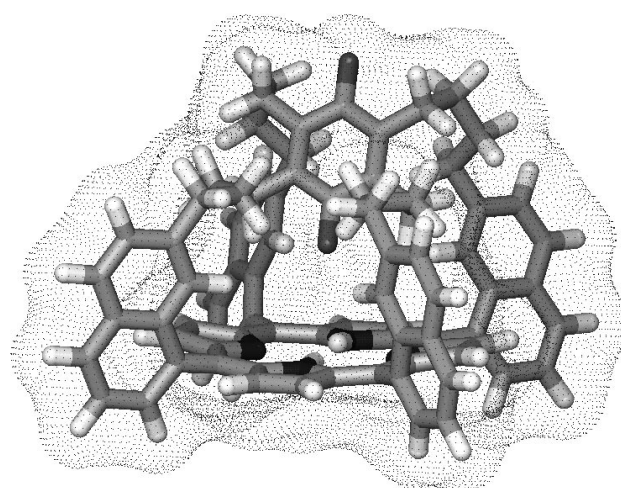


Figure 2. Calculated structure of the "naphthyl cage" with lowest potential energy.

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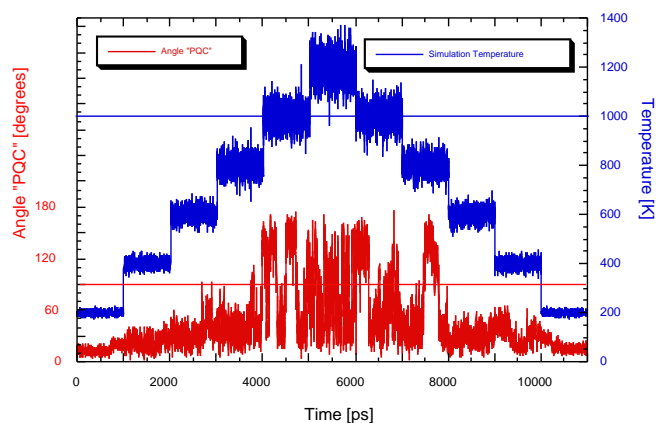


Figure 3. Simulated heating and annealing (equilibration time = 50 ps, simulation time for each temperature step = 1000 ps, temperature intervals = 200 K, maximum temperature = 1200 K). Definition of angle "PQC" see Figure 4.

to choose 1000 K as simulation temperature (Figure 3). The CFF91-forcefield [7] was used because it had been proven to reproduce well the Xray-structures of our porphyrin-quinone systems [4]. To analyse the dynamic behavior we defined internal coordinates by which the characteristic motions of the molecule can be described efficiently ("characteristical coordinates") (Figure 4). These "characteristical coordinates" were evaluated by statistical methods (frequency plots) (Figure 5). In addition we carried out conformational analysis on selected minimized structures with respect to the same internal coordinates (Figure 6). In contrast to the basic assumption we found that the "naphthyl cage" is not completely rigid. There is a characteristic dynamic process in the "naphthyl

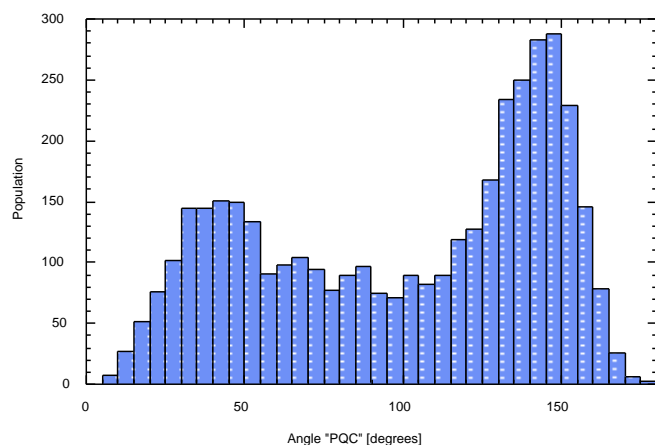


Figure 5. Histogram of angle "PQC" (1000 ps MD simulation, history = 0.25 ps, simulation temperature = 1000 K, sampling interval = 5 degrees)

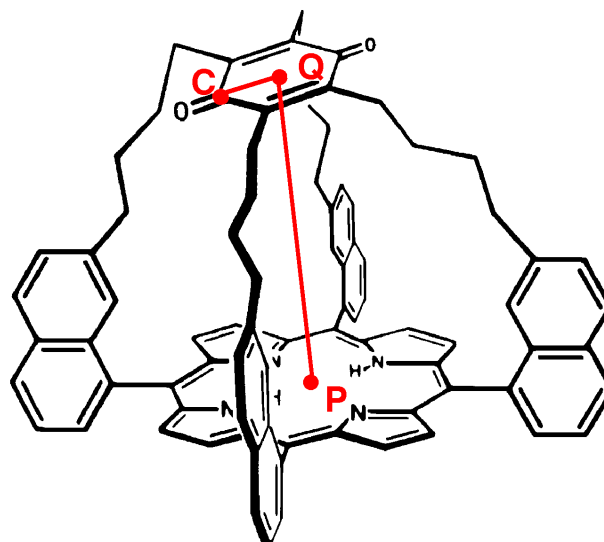


Figure 4. Definition of angle "PQC" which is the "characteristical coordinate" for the motion illustrated in Figure 7 (P: center of porphyrin, Q: center of quinone, C: carbon atom of quinone carbonyl group).

cage" (Figure 7). Nevertheless, the conformational mobility of the fourfold bridged porphyrin-quinone system is significantly decreased compared to the twofold bridged porphyrin-quinone system [4]. These calculated results exhibit good agreement with experimental results derived from temperature dependent $^1\text{H-NMR}$ experiments [3].

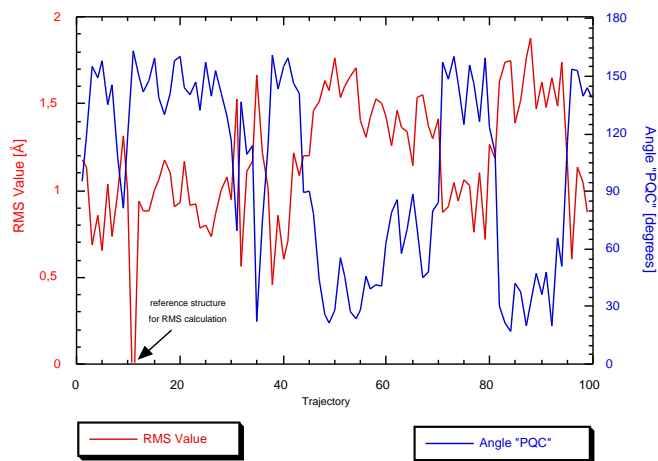


Figure 6: Relationship between RMS value (superimposition of all heavy atoms, reference structure: 11) and angle "PQC" of 100 minimized structures selected in regular intervals from the MD trajectory. It is evident that there is a direct correlation between the change of the RMS value and the change of the angle "PQC". Therefore the motion which is described by the change of the angle "PQC" should be the only significant motion which leads to a conformational change of the molecule.

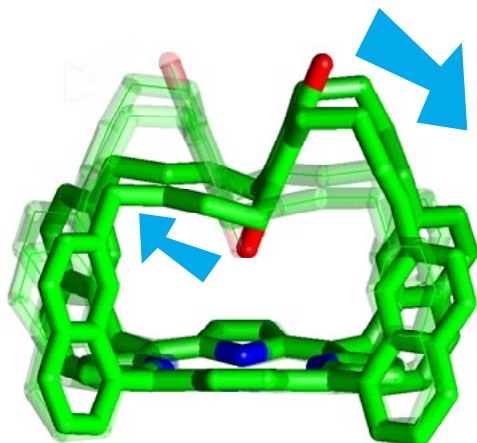


Figure 7. Characteristic dynamic process of the "naphthyl cage". The plane of the quinone moiety alternates between two positions with an effective rotation of about 120 degrees so that the carbonyl which points up in one conformer points down in the other conformer. The arrows indicate schematically the movement of the quinone oxygens.

Keywords: High-Temperature MD Simulations, Conformational Analysis, Porphyrin-Quinone Systems, Photosynthesis Models

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